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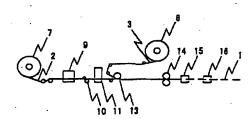
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## (54) SHEET TYPE HEATING ELEMENT AND METHOD OF MANUFACTURING THE SAME

(57) Water is adhered to the bottom face of a nonwoven fabric having a large number of pores, then a heat generating powder composition is sprayed onto the top face of this fabric to be held in place, then the top face of such non-woven fabric is superposed with another non-woven fabric(s) having a large number of pores and compressed, and thereafter, water or a solution of electrolytes in water is sprayed thereon.

Thereby, a sheet shaped heat generating body can be provided which uses a heat generating composition which generates heat by contacting with air, which causes no concentration of the heat generating composition in one direction, and which is thin, flexible and has good heat generating properties.

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#### Description

### Field of the Invention

The present invention broadly relates to sheet 5 shaped beat generating bodies, particularly to such thin and flexible heat generating sheets which reduce displacement and concentrated placement of heat generating composition, and the manufacturing method thereof.

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#### **Related Art**

Widely used as pocket heaters are heat generators which have as their main component oxidizable metals such as iron powder as one of the heating means, wherein the heat generating composition which contacts with oxygen in the air to emit heat is packed in air permeable bags.

Although these kinds of heat generators are advan- 20 tageous in that they may be used in a simple manner, they have problems in that when wearing the generator on the body, the heat generating composition moves down to the bottom of the bag due to their weight, not only during sports but also when standing still, so that 25 the change of shape causes an uncomfortable feeling to the wearer and the heat generating feature changes to become less effective.

Various efforts have been made to hold the heat generating composition in or between supporting members to form a sheet-like product as a means for reducing these defects.

Described below are examples of such efforts:

- a) A method of holding the heat generating compo- 35 sition with wire mesh or net shaped plastic objects (Patent Laid-Open Sho 53(1978)-84246 Publication):
- b) A method of superposing metal foils such as aluminum foils on non-woven fabric made of activated 40 carbon fiber and impregnated with chloride, water or other oxidation auxiliary agents (Patent Laid-Open Sho 63(1988)-37181 Publication);
- c) A method of spraying a heat generating agent on Japanese paper impregnated with an oxidation auxiliary agent, and thereafter subjecting it to pressure to mold such product into a sheet-like shape (Utility Model Sho 64(1989)-42018 Publication);
- d) A method of laying one over the other a plurality of non-woven fabric made of heat-fused fibers which may include plant fibers, and then distributing chemical heat generating agent therein (Patent Laid-Open Hei 2(1990)-142561 Publication); and e) A method of distributing heat generating agent on a supporting sheet which comprises unevenly layered fibers with a large number of very fine

pores, and to hold the agent thereon (Patent Laid-

Open Hei 3 (1991)-152894 Publication).

## Technical Problems to be Solved by the Invention

However, the related art described above has the following problems in the manufacturing process of the heat generating sheet or the resulting heat generator.

- a) When holding the generator with wire mesh or net shaped plastic objects, the rigidity of the sheetlike product is enlarged without achieving the softness required for practical use, and the heat generating composition powder becomes easily detached.
- b) in comparison to products using metal powders, the metal surface area is considerably small in products made by superposing metal foils such as aluminum foils on non-woven fabric made of activated carbon fibers, etc. impregnated with oxidation auxiliary agents, so that a good heat generating effect cannot be achieved. Also, increasing the number of foils results in increased thickness, reducing the flexibility of the product.
- c) Furthermore, products made by spraying the heat generating agent on paper which is then subjected to pressure to farm a sheet cause the heat generating agent to come off through folding or shaking, which is not practical.
- d) The combination of a plurality of non-woven fabrics by utilizing the water holding property of plant fibers and the heat fusion of synthetic fibers not only renders the structure and processing complicated, but also has practical problems in that the sheet-like object lacks flexibility due to instances where the non-woven fabrics do not adhere to each other, depending on the type and blending ratio of the heat fusive fibers and due to the rigid net-like structure in heat fusion.
- e) Concerning the method of distributing heat generating compositions on the supporting sheet made of irregularly layered fibers with a large number of very fine pores, this is a good method in that the composition may be distributed and held inside the pores in a homogenous manner. However, due to the fact that after securing the iron powder, a suspension liquid containing activated carbon, etc. is sprayed, it is difficult to hold the heat generating composition as a whole in a homogenous mixture.

As shown above, it is strongly desired to develop a flexible heat generating body, wherein the heat generating sheet is manufactured so as to allow easy and homogenous distribution and holding of the heat generating composition while preventing leakage of the powder, and a method of manufacturing the same.

### Summary of the Invention

The inventors of the present invention have repeated research aiming at solving the problems described above and to obtain a thin and soft heat gen3

erating sheet with a highly heat generative function, wherein the heat generating composition is securely held without being displaced, and as a result, have reached the conclusion that the objects can be achieved by dampening the bottom face of a multi-poric, non-woven fabric with water and thereafter spraying a heat generating powder composition from the top face of said non-woven fabric and holding such powder, reaching at the present invention.

In other words, the present invention is a) a heat generating sheet characterized in that after adhering water to the bottom face of a non-woven fabric a, a heat generating powder composition is sprayed on the top face of such fabric a and held inside its pores, the top face of the non-woven fabric a is superposed with nonwoven fabric b, then compressed via a mold compressor to form a sheet product, which is then impregnated with water or a solution of electrolytes in water, and the manufacturing method thereof; b) a heat generating sheet characterized in that water is adhered to the bottom face of a multi-poric, non-woven fabric a and/or the top face of a non-woven fabric c, then non-woven fabric c is superposed on the bottom face of non-woven fabric a, then a heat generating powder composition is sprayed onto the top face of non-woven fabric a and held inside the pores, then said non-woven fabric b is superposed on the top face of said non-woven fabric a, then compressed via a mold compressor to form a sheet product, which is then impregnated with water or a solution of inorganic electrolytes in water, and the manufacturing method thereof; c) a heat generating sheet characterized in that a plurality of layers of nonwoven fabric in a combination of non-woven fabrics a and b and/or a combination of non-woven fabrics c, a, b are superposed via water adhesion or water adhesion plus compression, and at least one of said non-woven fabric layers hold the heat generating composition, and the manufacturing method thereof.

The present invention holds the heat generating composition with non-woven fabric a by moistening the bottom face of non-woven fabric a and spraying the heat generating powder composition from the top face, thereby causing homogeneous holding of the powder in the non-woven fabric without leakage, and by superposing non-woven fabric b thereon and the like and compressing them, the non-woven fabrics do not separate, securing the fixing of the sheet shape, and providing a heat generating composition which is thin and flexible.

### Brief Description of the Drawings

Fig. 1 is a cross sectional, view of heat generating sheet 1.

Fig. 2 is a cross sectional view of heat generating sheet 1'.

Fig. 3 discloses the first example for performing the steps of the present invention.

Fig. 4 discloses the second example for performing the steps of the present invention.

Fig. 5 discloses the third example for performing the steps of the present invention.

Fig. 6 is a diagram showing the heat generative properties of the present invention.

Fig. 7 is a cross sectional view of a plaster-type, sheet-shaped pocket heater.

### Embodiments of the Invention

The present invention may be applied to heat generators for use of warming the human body, warming animals and plants, heating and warming foods, and also heating and warming machines and equipment, etc., and the manufacturing method of such generators.

The non-woven fabric used in the present invention is a multi-poric, non-woven fabric, which has the property of being able to hold such heat generating composition material described below which is a material mixture used in powder form (hereinafter referred to as "powder composition") inside its pores, having a great moisture holding capacity, and is mainly composed of plant fibers such as pulp, cotton and linen, or recycled fibers such as rayon. In addition, a mixture of plant fibers or recycled fibers with a slight amount of synthetic fibers such as nylon, polyester, acryl or polyolefin may be used, too. Among these materials, preferable is a non-woven fabric wherein the total sum of plant fibers and recycled fibers is 95% or more of the fiber content, because of their large moisture holding capacity and their ability to maintain the flexibility of the sheet without causing beat fusion when heating the product to compress and mold a sheet-shaped product. More preferably, the product utilizes a non-woven fabric which contains 98% or more of pulp, cotton, linen or rayon,

There are no particular limits to the method of manufacturing non-woven fabric a, which may be formed by an entanglement of fiber materials, or formed by using a small amount of adhesive agent or synthetic resin, etc, as binder. The greater the porosity rate of non-woven fabric a, the easier the distribution of the powder composition into the pores, but as pores which are too large incur leakage of the powder, the porosity race is normally 70 - 99.5%, preferably 80 - 99%.

The thickness of non-woven fabric a is normally 0.5 - 25mm depending upon the amount of heat generating composition to be held, and the porosity rate of non-woven fabric a, preferably 1 - 10mm. The measuring weight is normally 5 - 200 g/m², preferably 30 - 150 g/m².

In the present invention, the spraying of the composition material on the top face of non-woven fabric a is conducted such that water is adhered to the bottom face of non-woven fabric a, and then the composition material is sprayed thereon, By causing water to adhere to the bottom face of non-woven fabric a, even large-pored, non-woven fabrics can hold powder due to the adhesion of water and prevent leakage.

The amount of water to adhere to the bottom face of

non-woven fabric a need only be such so as to prevent leakage of powder composition from the bottom face of non-woven fabric a by the moisture, which is normally 10 - 200 g/m² depending upon the measuring weight, thickness and material quality, etc. of the non-woven fabric a, and preferably 20 - 120 g/m².

The water adhesion method need only be such so as to enable adjustment of the amount of the adhering water and a homogenous adhesion, for example the method of atomizing or sticking water with a roll on the bottom face of non-woven fabric a.

In the present invention, the material composing the powder composition is, for example, oxidizable metal powder, activated carbon, water-holding agent.

Concerning the inorganic electrolytes, they are one component of the powder composition if mixed as solid body into the materials above, and if sprayed and impregnated in the form of aqueous solution after the molding of the sheet, for example, they are not included into the powder composition.

The oxidizable metal powder is iron powder and aluminum powder, etc., but normally, iron powder is used, namely reduced iron powder, atomized iron powder, electrolytic powder, etc.

Activated carbon is used as the reactive agent and also as the water holding agent, and is normally palm activated carbon, wood flour carbon, or peat carbon, etc.

The inorganic electrolytes used are preferably chlorides of alkali metals, alkali earth metals and heavy metals, and sulfates of alkali metals, for example sodium chloride, potassium chloride, calcium chloride, magnesium chloride, ferric chloride, sodium sulfate, etc.

As the water holding agent is used pearlite powder, vermiculite, macromoleculic water holding agent, etc., but is preferably a macromoleculic water holding agent.

The particle size of the powder composition is normally not more than 60 mesh, preferably containing at least 50% of particles which are not larger than 100 mesh.

The heat generating composition is made by adding and mixing water or a solution of inorganic electrolytes in water to the powder composition described above. The blending ratio in the whole of the heat generating composition cannot be specified in general, as it depends upon the properties and shape of the non-woven fabric and the heat generating function to be achieved, but to give one example, when setting the oxidizable metal powder as 100% by weight, the activated carbon may be 5 - 20% by weight, the inorganic electrolytes 1.5 - 10% by weight, and water 25 - 60% by weight.

In addition, it is also possible to mix water holding agents such as pearlite powder, vermiculite or macromoleculic water holding agent, or hydrogen generation depressor or consolidation preventor, as desired.

Among those described above, the water, or the water and inorganic electrolytes will be supplied after the molding into a sheet shape.

Examples of the method of holding the heat gener-

ating composition inside the pores of the non-woven fabric a are as follows: a) spraying the mixture of powder material such as iron powder, activated carbon, inorganic electrolytes and the like on the non-woven fabric a, then subjecting the fabric to vibration to cause the mixture to proceed inside the pores to be held therein; or b) spraying the mixture of powder materials with exception of the inorganic electrolytes such as iron metals and activated carbon onto the top of non-woven fabric a, subjecting the fabric to vibration to cause the mixture to proceed inside the pores to be held therein, then, after the molding to a sheet shape, spraying such inorganic electrolytes as a solution in salt water. In both cases a) and b), the alternative to subjecting the fabric to vibration is to subject the non-woven fabric a to suction from the bottom direction, thereby causing distribution and holding of the powder.

Among these two, method b) is preferable in that the inorganic electrolytes can be distributed on the whole surface in a homogenous manner.

As stated above, by causing water to stick to the bottom face of non-woven fabric a and spraying and holding the powder composition, the composition material itself is secured by the adhesion of water to the wet bottom face of non-woven fabric a, so that the distribution of powder composition tends to increase from the bottom face of the non-woven fabric a to its top face.

The amount of heat generating composition to be held inside the non-woven fabric to the non-woven fabric depends upon the thickness of the non-woven fabric, the final thickness of the heat generator and the desired heat generating effects, etc., but is normally 150 - 10,000 g/m<sup>2</sup> of supportive body, and preferably 1,000 - 5,000 g/m<sup>2</sup>.

If the held amount is less than 150g, the generated heat temperature and duration of the generated heat are reduced, but when the held amount exceeds 10,000g, the heat generator becomes thicker, so that the molding of a thin and flexible sheet becomes difficult.

Non-woven fabric b functions to hold the powder composition remaining on the top face of non-woven fabric and to prevent leakage of the powder composition from the top face, so that preferably, it has a large water holding capacity and has no heat fusion property, so that it is a non-woven fabric made of the same material as that of non-woven fabric a, namely pulp, cotton, linen or rayon, etc.

In the event the porosity rate of non-woven fabric b is too large, the powder is likely to leak, so it is desirably slightly smaller than that of non-woven fabric a, normally 60 - 99%, and preferably 70 - 98%.

The thickness of non-woven fabric b depends upon the porosity rate of non-woven fabric b and the amount of powder composition held, and is normally 0.1 - 10mm, preferably 0.5 - 5mm. The measuring weight is normally 5 - 150g/m², and preferably 20 - 100g/m².

In the present invention, the layered product containing non-woven fabric a which holds the powder com-

position and non-woven fabric b is compressed by a compressor and processed into the shape of a sheet.

The compression may be conducted by utilizing a pressing machine or pressing roll on the layered product containing non-woven fabric a which holds the powder composition and non-woven fabric b.

The compression may be conducted by using a plane or flat roll, but in order to prevent separation of the compressed sheet in the non-woven fabrics a and b, it is preferable to form protrusions in the shape of waves, turtlebacks, rings, polka dots, stitch designs or others to form an embossed face.

The compressing may be conducted under heating. Heat compressing is advantageous in that the moisture heating secures the fixing of the shape even more.

The compression temperature and pressure depend upon the material qualities of non-woven fabrics a and b and the amount of powder composition to be held, which cannot be specified in general, but for example, when using a heating roll with embossed face, the temperature normally ranges from ordinary temperature up to 300° C, and the linear pressure from around 0.5 through 300kg/cm, In this way, the shaped of the load is secured in the compressed state, forming a thin sheet.

The thickness of the heat generating sheet will be selected according to the heat generation to be achieved and the use, but in order to utilize the properties as a sheet to design them as thin as possible, they are normally 6mm or less, preferably 4mm or less. Concerning the size, the sheet will be cut in appropriate sizes according to the purpose of use.

The amount of the water or the solution of inorganic electrolytes in water with which the sheet product is either to be impregnated with the amount of the water set as one component of the heat generator, or the total amount of water and inorganic electrolytes, and these will be supplied through atomization or roll adhesion.

The thus obtained sheet-like heat generator is stored in this state, or, in order to obtain those heat generating properties corresponding to its use, in a bag made of laminated film of polyethylene having permeable pores and non-woven fabric, or a bag made of a permeable film with micropores, then sealed in a non-permeable bag for storage, to be used as pocket heaters or medical heat generating bags.

In addition, the bag may also be used for warming animals and plants, heating and warming foods, and heating and warming machines and equipment, etc.

In the present invention, when holding the powder composition in the non-woven fabric a, it is possible to superpose a fine, non-woven fabric c on the bottom face of non-woven fabric a for the purposes of securely preventing powder from falling out of non-woven fabric a even when the pores of non-woven fabric a are large.

Used as materials for non-woven fabric c are materials mainly composed of pulp, cotton, linen, rayon and other fibers, namely non-woven fabric made of pulp, cotton, linen, or rayon, etc. and paper-like products such as

tissue paper.

The measuring weight of non-woven fabric c is normally 5 - 150g/m<sup>2</sup>, and preferably 10 - 100g/m<sup>2</sup>.

When superposing non-woven fabric c on the bottom face of non-woven fabric a, water may be applied to the bottom face of non-woven fabric a and/or the top face of non-woven fabric c and then superposed. By thus superposing non-woven fabrics a and c in a moist state, they are superposed in a close manner through their moisture adhesion, requiring no adhesive agent, which is a great advantage.

The amount of water to be applied to the non-woven fabric is normally 10 - 200g/m<sup>2</sup>, and preferably 20 - 150 g/m<sup>2</sup>.

By superposing the non-woven fabrics a and c in a moist state, both are superposed in a close manner through their wetness adhesion, enabling the sheet molding without requiring any adhesive agent, which is a great advantage.

In the present invention, when superposing nonwoven fabric b on the top face of non-woven fabric a, water may first be adhered to the bottom face of nonwoven fabric b, and thereafter be superposed. The method of adhering water to non-woven fabric b may be realized through water atomizing or roll adhesion, and the applied amount is normally 15 - 300 g/m², preferably 30 - 200g/m².

Instead of adhering water to non-woven fabric b, it may be adhered to the top face of non-woven fabric a, or on both non-woven fabrics a and b. When adhering water to the top face of non-woven fabric a, a portion of the powder composition may scatter when using certain adhesion methods, so that the method of adhesion to non-woven fabric b is preferable.

When superposing non-woven fabrics a and b with the appliance of water, the fabrics are superposed closely onto each other due to wetness adhesion, which not only prevents the heat generating powder composition material from scattering, but also allows smooth introduction into the compressor, and when using a heating compressor, the moist heating effect allows a secure fixing of the shape, which are great advantages.

According to the present invention, the sheet made of non-woven fabrics a and b, and the sheet made of non-woven fabrics a, b, and c are sheet products superposed through water adhesion and compression adhesion.

By superposing a plurality of these heat generating sheets, a product may be made by superposing a plurality of layers of heat generating sheets. During the manufacture process of the sheet product, it is also possible to pile the non-woven fabrics as c-a-b-a-b from the bottom, or as c-a-a-a-b From the bottom, and cause the powder composition to be mainly held with the non-woven fabric a.

By superposing a plurality of layers as described above, the thickness of the heat generator may be determined arbitrarily. The plurality of layers are superposed by water adhesion, or water adhesion plus compression adhesion, while at least one of such layers is a heat generator holding heat generating powder composition, which avoids a strong three-dimensional wired structure, so that it is an effective heat generator which keeps flexibility.

# Preferred Embodiments

Now, the present invention will be exemplified with reference to the drawings, and explained more specifically. Furthermore, the present invention is not limited to the embodiments.

Fig.1 is a cross sectional view of a heat generating sheet 1 according to the present invention.

Fig.2 is a cross sectional view of a heat generating sheet 1' carried out in a different mode from that of Fig.1.2 indicates a non-woven fabric a, 3 indicates non-woven fabric b. 4 indicates the heat generating composition held in non-woven fabric a (2). 5 indicates the heat generating composition held in non-woven fabric b(3). 6 indicates non-woven fabric c.

Fig. 3 discloses a first example for performing the steps of the present invention. 7 in Fig. 3 is a roll of non-woven fabric a (2) for use with the present invention, 8 is a roll for non-woven fabric b(3). Water is applied to non-woven fabric a (2) on its bottom face by a water atomizer 9, and this non-woven fabric a (2) is subjected to roll 10, then sprayed with the powder composition at powder filler 11, then subjected to vibration to hold the heat generating composition inside the pores of non-woven fabric a (2).

Then, non-woven fabric b(3) is superposed via roller 13, heat compressed at compressor 14, cut into the desired size at cutter 15, then sprayed with a solution of inorganic electrolytes in water at salt water sprayer 16 to finally form heat generating sheet 1.

Figs. 4 and 5 illustrate second and third examples for performing the steps of the present invention when superposing non-woven fabric c(6) on the bottom face of non-woven fabric a(2).

The heat generating sheet obtained as above is packed in bags with adjusted permeability in accordance with their use, and used as pocket heaters or medical equipment by successively utilizing the method of sealing such sheet in non-permeable bags.

Fig. 7 is a cross sectional view of a plaster-type pocket heater using a heat generator sheet according to the present invention. 19 indicates the inner bag, 20 the layer of bonding agent, 21 the separating paper and 22 the outer bag.

### Embodiment 1

In the device shown in Fig. 3, a non-woven fabric with approximately 1.9mm thickness,  $57g/m^2$  measuring weight and porosity rate 97.9% made of wooden pulp (Habix K.K.; "J Soft") was sent with 12.3m/min speed, and water was homogeneously atomized on the bottom face of the non-woven fabric at a rate of  $35g/m^2$ .

Then, a mixture of 90% iron powder. 8% activated carbon, 2% macromoleculic water holding agent was sprayed from the top face of the non-woven fabric at a rate of 1,100g/m², and at the same time, the non-woven fabric was shaken up and down to hold such mixture in its pores. Thereafter, a non-woven fabric made of wooden pulp with thickness 1.1mm, measuring weight 40g/m², and porosity rate 97.6% (Honshu Seishi K.K., "Kinokurosu") was superposed on the top face of the non-woven fabric above, and the sheet was put through a heat compressing roller with an embossed face with striped design on the roller face, and set at 195°C, linear pressure 40kg/cm to form the shape of a sheet.

Then, the sheet product was cut in the size of 8.5cm × 12.5 cm. Thereafter, a salt water solution which is a mixture of 8.5% sodium chloride and 91.5% water was sprayed at the rate of 520g/m² to obtain an approximately 2 mm thick heat generating sheet. This heat generator is flexible and permits no falling of the heat generating composition. This heat generator was stored in a flat shaped inner bag, of which one face is composed of a multi-layered sheet with a microporic film made of polypropylene with 350g/m² day moisture permeability and a nylon non-woven fabric, and of which the other face is composed of a laminated film of polyethylene film and nylon non-woven fabric to form the heat generating sheet. This was further sealed in a non-permeable bag, then stored.

After two days, the heat generating sheet was taken out of the outer bag and indoor measurements were conducted concerning the heat-generating effect based on the JIS S-4100 heat generation test method at room temperature 20°C and relative humidity 65%. As a result, the heat generating effect as shown in Fig. 6 was obtained.

The temperature exceeded 40°C after 8.5 minutes, and reached 52°C in 70 minutes. The duration of heat generation for 40°C or more was approximately 10 hours.

Furthermore, when taking this heat generating sheet out of the outer bag and wearing it on the body, a comfortable temperature could be obtained for around 12 hours, while always maintaining a flexible sheet shape.

# Embodiment 2

In the device shown in Fig. 4, a non-woven fabric with approximately 1.9mm thickness, 57g/m² measuring weight and 97.9% porosity rate made of wooden pulp (Habix K.K.; "J Soft") was sent with 12.3m/min speed, and water was homogeneously atomized on the bottom face of the non-woven fabric at a rate of 40g/m². Then, after superposing a tissue paper of 30g/m² measuring weight on the bottom face of the non-woven fabric, a mixture of 90% iron powder, 8% activated carbon, 2% macromoleculic water holding agent was sprayed from the top face of the non-woven fabric at a rate of 1,100g/m², and at the same time, the non-woven fabric

was shaken up and down to hold such mixture in its pores. Thereafter, on the top face of the fabric above, a non-woven fabric made of wooden pulp with thickness 1.1mm, measuring weight 40g/m², and 97.6% porosity rate (Honshu Seishi K.K.; "Kinokurosu") was superposed after having water adhered thereto at its bottom face at the rate of 60g/m².

Thereafter, the heat generating sheet was obtained in the same way as in Embodiment 1.

This heat generator is flexible and there was no falling of the heat generating composition. This heat generating sheet was stored in a flat inner bag, of which one face is a multi-layered sheet of microporic propylene film with a moisture permeability of 350g/m² day and a nylon non-woven fabric, and of which the other face is a laminated film of polyethylene and nylon non-woven fabric to form a sheet-shaped heat generating bag. This bag was further sealed in a non-permeable outer bag.

After two days, the heat generating sheet was taken out from the outer bag and measurements made with regard to its heat generating effect in the same way as in Embodiment 1. As a result, the temperature exceeded 40° C after 9 minutes, and reached 52°C in 65 minutes. The duration of heat generation of 40°C or more was approximately 11 hours.

Furthermore, when this heat generating sheet was taken out of the outer bag and worn on the body, a comfortable temperature could be obtained for around 12 hours, while always maintaining a flexible sheet shape.

## **Embodiment 3**

Using the device shown in Fig.5, the water atomization on the bottom face of the non-woven fabric ("J Soft") was replaced with the following: 30 g/m² water was atomized on the top face of a tissue paper with measuring weight 30 g/m² to moisten the paper, which was then superposed on the bottom face of a non-woven fabric ("J Soft") to obtain the heat generating sheet in the same way as in Embodiment 2.

This heat generator was flexible and allowed no falling of the heat generating composition.

### **Embodiment 4**

In the device shown in Fig. 4, a non-woven fabric made of wooden pulp with approximately 1.2mm thickness and 40g/m² measuring weight (Honshu Seishi K.K.; "Kinokurosu") was sent with 12.3m/min speed, and water was homogeneously atomized on the bottom face of the non-woven fabric at a rate of 35g/m². Then, after superposing a tissue paper of 27g/m² measuring weight on the bottom face of the non-woven fabric, a mixture of 90% iron powder, 8% activated carbon, 2% macromoleculic water holding agent was sprayed from the top face of the non-woven fabric at a rate of 1,430g/m², and at the same time, the non-woven fabric was shaken up and down to hold such mixture in its pores. Thereafter, on the top face of this fabric, a non-

woven fabric made of wooden pulp with thickness 1.5mm and measuring weight  $60g/m^2$  (Honshu Seishi K.K., "Kinokurosu") was superposed after having water adhered thereto at its bottom face at the rate of  $60g/m^2$ . This sheet was put through a heat compressing roller with an embossed face with striped design on the roller face and set at  $200^{\circ}$ C, linear pressure 166kg/cm to form the shape of a sheet.

In order to measure the flexibility of this sheet, a test piece of 25mm width and 88mm length was cut therefrom, and, using the Galle method set forth in JIS L-1096 and a bending repulsion test unit, the bending repulsion of this sheet was measured.

Also, salt water which is a mixture of 8.5% sodium chloride and 91.5% water was sprayed on the sheet at the rate of 608g/m<sup>2</sup>, then a test piece was immediately cut therefrom and the bending repulsion measured. As a result, the bending repulsion before spraying of the salt water was 1217mgf, and that after the spraying of the salt water was 1450 mgf.

Thereafter, the heat generating sheet was obtained in the same way as in Embodiment 1 with the exception that the salt water to be sprayed was 608 g/m<sup>2</sup>.

This heat generator is flexible and there was no falling out of the heat generating composition. This heat generating sheet was stored in a flat inner bag, of which one face is composed of a multi-layered sheet of microporic film made of polypropylene with a moisture permeability of 350g/m² day and a nylon non-woven fabric, and of which the other face is composed of a laminated film of polyethylene and nylon non-woven fabric with an additional layer of adhesive agent and separation paper superposed thereon to form a sheet-shaped heat generating bag. This bag was further sealed in a non-permeable outer bag.

After two days, the heat generating sheet was taken out from the outer bag and measurements made with regard to its heat generative effect in the same way as in Embodiment 1. As a result, the temperature exceeded 40°C after 8 minutes, and reached 52°C in 65 minutes. The duration of heat generation for 40°C or more was approximately 12 hours.

Furthermore, when this heat generating sheet was taken out of the outer bag and worn on the body, a comfortable temperature could be obtained for around 12 hours, while always maintaining a flexible sheet shape.

## Comparative Example 1

In the device shown in Fig. 4, a non-woven fabric with approximately 2.5mm thickness, 38g/m² measuring weight and 95.7% porosity rate made of 50% polyester and 50% heat fusion polyester (Marusan Sangyo K.K.; "Estermelty") was sent with 12.3m/min speed, and water was homogeneously atomized on the bottom face of the non-woven fabric at a rate of 40g/m². Then, after superposing tissue paper of 27g/m² measuring weight on the bottom face of the non-woven fabric, a mixture of 90% iron powder, 8% activated carbon, 2% macromole-

culic water holding agent was sprayed from the top face of the non-woven fabric at a rate of 1,430g/m². and at the same time, the non-woven fabric was shaken up and down to hold such mixture in its pores. Thereafter, on the top face of this fabric, a non-woven fabric made of wooden pulp with thickness 1.5mm and measuring weight 60g/m² (Honshu Seishi K.K.; "Kinokurosu") was superposed after having water adhered thereto at its bottom face at the rate of 60g/m². This sheet was put through a heat compressing roller with an embossed face with striped design on the roller face, and set at 200°C and linear pressure 166kg/cm to form the shape of a sheet.

The same flexibility test as with Embodiment 4 was carried out for this sheet. As a result, the bending repulsion before spraying of the salt water was 2647mgf, and that after the spraying of the salt water was 2267mgf.

Thereafter, the heat generating sheet was obtained in the same way as in Embodiment 4.

This heat generator shows no falling out of the heat generating composition, but is hard compared to the heat generating sheet of Embodiment 4 and shows low flexibility.

This heat generating sheet was scored in a flat inner bag, of which one face is composed of a multi-layered sheet of microporic propylene film with a moisture permeability of 350g/m² day and a nylon non-woven fabric, and of which the other face is composed of a laminated film of polyethylene and nylon non-woven fabric with an additional layer of adhesive agent and separation paper superposed thereon to form a sheet-shaped heat generating bag. This bag was further sealed in a non-permeable outer bag.

After two days, the heat generating sheet was taken out of the outer bag and continued to hold a comfortable temperature when worn on the body and maintained the sheet shape, but was always hard, causing an uncomfortable feeling.

#### Claims

- A sheet shaped heat generating body comprising a sheet product impregnated with water or a solution of inorganic electrolytes in water, wherein said sheet product includes:
  - a porous, first non-woven fabric with water adhered to its bottom face;
  - a heat generating powder composition sprayed on the top face of said first non-woven fabric to be held inside the pores thereof; and
  - a second non-woven fabric superposed on the top face of said first non-woven fabric,
  - said sheet product being made by compressing said non-woven fabrics via a mold compressor. 55
- A sheet shaped beat generating body comprising a sheet product impregnated with water or a solution of inorganic electrolytes in water, wherein said

sheet product comprises:

a first non-woven fabric;
a third non-woven fabric superposed on the bottom face of said first non-woven fabric;
a second non-woven fabric superposed on the top face of said first non-woven fabric; and a heat generating powder composition from the top face of said first non-woven fabric to be held inside the pores of the fabric, the bottom face of said first non-woven fabric and the top face of said third non-woven fabric being bonded by water adhesion, and said second non-woven fabric being superposed on the top face of said first non-woven fabric and subsequently compressed via a

mold compressor to form said sheet product.

- A sheet shaped heat generating body characterized in that a plurality of non-woven fabrics are mutually superposed via water adhesion or water adhesion plus compression, and that at least one of said non-woven fabrics holds a heat generating composition inside its pores.
- 4. A sheet shaped heat generating body according to Claim 1 or 2, wherein said first non-woven fabric has as its main component fibers selected from pulp, cotton, linen and rayon, and wherein the porosity rate is 60 - 99.5%, the thickness is 0.5 -25mm and the measuring weight is 5 - 200 g/m².
- A sheet shaped heat generating body according to Claim 1 or 2, wherein said second and/or third nonwoven fabric has as its main component fibers selected from pulp, cotton, linen and rayon, and wherein the measuring weight is 5 - 150g/m².
- 6. A sheet shaped heat generating body according to any one of Claims 2 through 5, wherein said heat generating powder composition has as its main components iron powder and activated carbon, or iron powder, activated carbon and inorganic electrolytes, etc. and includes a solid component which contacts with the oxygen in air to generate heat.
  - 7. A sheet shaped heat generating body according to Claim 1 or 2, wherein said first and second nonwoven fabrics are superposed by adhering water on the top face of said first non-woven fabric and/or bottom face of said second non-woven fabric.
  - A sheet shaped heat generating body according to Claim 5, wherein the amount of water to be adhered is 10 - 200g/m².
  - A sheet shaped heat generating body according to any one of Claims 1 through 3, wherein the compressed face of said non-woven tabric has a joggle

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face composed of the embossed face of a compression roll.

10. A method of manufacturing a sheet shaped heat generating body, characterized in that:

water is adhered to the bottom face of a porous, first non-woven fabric; then, a heat generating powder composition is sprayed on the top face of said first non-woven fabric to be held inside its pores; then, a second non-woven fabric is superposed on the top face of said first non-woven fabric and subsequently compressed via a mold compressor to form a sheet product; and 15 then, impregnating said sheet product with water or a solution of inorganic electrolytes in

11. A method of manufacturing a sheet shaped heat 20 generating body, characterized in that:

water is adhered to the bottom race of a porous, first non-woven fabric and/or the top face of a third non-woven fabric;

then, said third non-woven fabric is superposed on the bottom face of said first non-woven fabric;

then, a heat generating powder composition is sprayed on the top face of said first non-woven fabric to be held inside its pores;

then, a second non-woven fabric is superposed on the top face of said first non-woven fabric and subsequently compressed via a mold compressor to form a sheet product; and then, impregnating said sheet product with water or a solution of inorganic electrolytes in

12. A method of manufacturing a sheet shaped heat 40 generating body, characterized in that:

water.

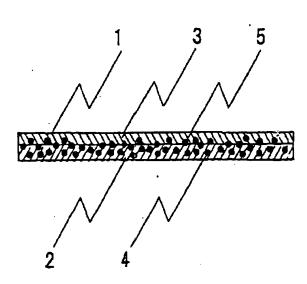
a plurality of layers of non-woven fabric in a combination of a first and second non-woven fabrics or a combination of a first, second and 45 third non-woven fabrics are superposed via water adhesion or water adhesion plus compression, and

at least one of said non-woven fabrics hold a heat generating composition inside its pores.

13. A method of manufacturing a sheet shaped heat generating body according to any one of the Claims 10 through 12, wherein said first non-woven fabric has as its main component fibers chosen from pulp, cotton, linen and rayon, and wherein the porosity rate is 60 - 99.5%, the thickness is 0.5 - 25mm, and the measuring weight is 5 - 200 g/m<sup>2</sup>.

- 14. A method of manufacturing a sheet shaped heat generating body according to any one of Claims 10 through 12, wherein said second and/or third nonwoven fabrics have as their main components fibers selected from pulp, cotton, linen and rayon, and wherein the measuring weight is 5 - 150 g/m<sup>2</sup>.
- 15. A method of manufacturing a sheet shaped heat generating body according to any one of Claims 10 through 12, wherein said heat generating powder composition has as its main component iron powder and activated carbon, or iron powder, activated carbon and inorganic electrolytes, and includes a solid component which contacts with the oxygen in air to generate heat.
- 16. A method of manufacturing a sheet shaped hear generating body according to any one of Claims 10 through 12, wherein said first and second nonwoven fabrics are superposed by adhering water to the top face of said first non-woven fabric and/or the bottom face of said second non-woven fabric.
- 17. A method of manufacturing a sheet shaped heat generating body according to Claim 16, wherein the amount of water adhered to the bottom face of said first non-woven fabric and/or the top face of said second non-woven fabric is 10 - 200g/m².
- 18. A method of manufacturing a sheet shaped heat generating body according to any one of Claims 10 through 12, wherein said mold compressor has embossing on at least one of its compressing faces.

F.g.1



Fizz

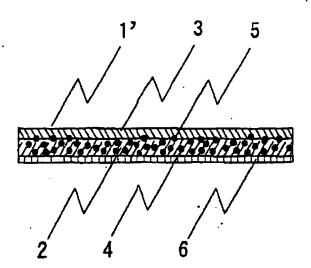
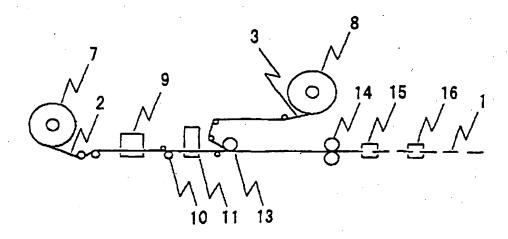
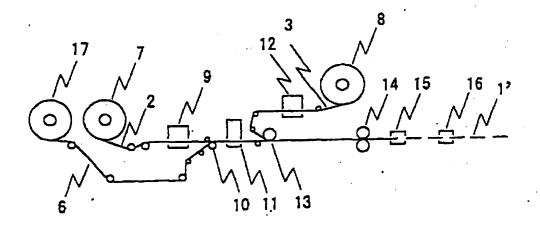


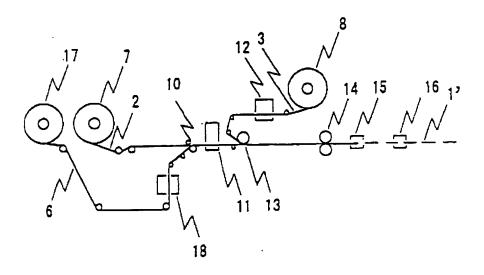
Fig 3

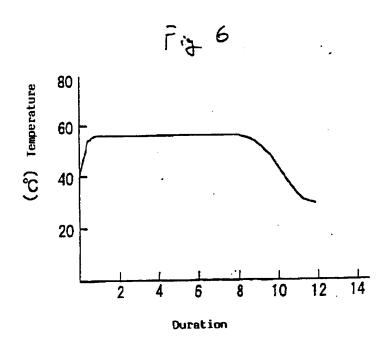


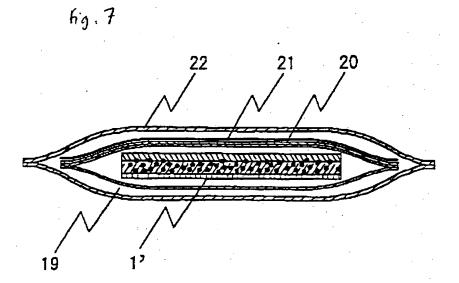
Fiz 4











#### EP 0 786 240 A1

# INTERNATIONAL SEARCH REPURT International application No. PCT/JP95/02108 CLASSIFICATION OF SUBJECT MATTER Int. Cl 6 A61F7/08 According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int. Cl<sup>6</sup> A61F7/08 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched 1926 - 1995 Jitsuyo Shinan Koho 1971 - 1995 Kokai Jitsuyo Shinan Koho Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. Category\* 1-9 JP, 7-59809, A (Nippon Pionix K. K.), EA March 7, 1995 (07. 03. 95), Lines 37 to 47, column 3, lines 1 to 33, column (Family: none) JP, 2-142561, A (Takashi Seike), May 31, 1990 (31. 05. 90), 1-9 Α Line 12, lower right column, page 1 to line 4, upper left column, page 2, line 9, upper left column, page 3, lines 4 to 13, upper right column, page 3, line 9, lower right column, page 3 (Family: none) See patent family annex. Further documents are listed in the continuation of Box C. later document published after the international filing date or priority date and not in conflict with the application but cited to understand Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "E" earlier document but published on or after the international filling date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special remon (as specified) document of particular relevance; the claimed invention cannot be considered to involve as inventive step when the document is combined with one or more other such documents, such combination being obvious to a purson skillind in the art "O" document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of mailing of the international search report Date of the actual completion of the international search December 19, 1995 (19. 12. 95) November 28, 1995 (28. 11. 95) Authorized officer Name and mailing address of the ISA/ Japanese Patent Office

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